Magnetic anisotropy of the van der Waals ferromagnet $\text{Cr}_2\text{Ge}_2\text{Te}_6$ studied by angular-dependent x-ray magnetic circular dichroism

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The van der Waals ferromagnet $\text{Cr}_2\text{Ge}_2\text{Te}_6$ (CGT) has a two-dimensional crystal structure where each layer is stacked through van der Waals force. We have investigated the nature of the ferromagnetism and the weak perpendicular magnetic anisotropy (PMA) of CGT by means of x-ray absorption spectroscopy and x-ray magnetic circular dichroism (XMCD) studies of CGT single crystals. The XMCD spectra at the Cr $L_{2,3}$ edge for different magnetic field directions were analyzed on the basis of the cluster-model multiplet calculation. The Cr valence is confirmed to be 3+ and the orbital magnetic moment is found to be nearly quenched, as expected for the high-spin t_{2g}^3 configuration of the Cr^{3+} ion. A large (~ 0.2 eV) trigonal crystal-field splitting of the t_{2g} level caused by the distortion of the CrTe_6 octahedron has been revealed, while the single-ion anisotropy (SIA) of the Cr atom is found to have a sign *opposite* to the observed PMA and too weak compared to the reported anisotropy energy. The present result suggests that anisotropic exchange coupling between the Cr atoms through the ligand Te $5p$ orbitals having strong spin-orbit coupling has to be invoked to explain the weak PMA of CGT, as in the case of the strong PMA of CrI_3 .

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I. INTRODUCTION

The discovery of graphene has invoked renewed interest in the studies on two-dimensional (2D) materials including layered transition-metal chalcogenides [1–4]. The 2D materials show various fascinating properties that may lead to applications for new spintronics devices. In addition, the relation between dimensionality and various physical properties has long been a major subject from a fundamental point of view. For instance, the Mermin-Wagner theorem states that a long-range magnetic order in the 2D isotropic Heisenberg model cannot be realized at finite temperature due to long-range magnetic fluctuations [5]. Recently, van der Waals (vdW) ferromagnets, which have 2D crystal structures but show ferromagnetic order [6], such as $\text{Cr}_2\text{Ge}_2\text{Te}_6$ (CGT) [7–17] and CrI_3 [18,19], have attracted great interest. Although the

magnetism of a few- to several-monolayer CGT shows soft behaviors well described by the 2D Heisenberg model [12], the finite Curie temperature of 61 K [7,10,11] and the easy magnetization axis along the c -axis (out-of-plane) direction [7,9,11] indicate a finite perpendicular magnetic anisotropy (PMA) and hence a departure from the 2D Heisenberg model. On the other hand, CrI_3 exhibits ferromagnetism down to monolayer thickness, which suggests a stronger PMA than CGT and is well described by the 2D Ising model [18].

The magnetic anisotropy of a 2D ferromagnet arises primarily from (i) the single-ion anisotropy (SIA) of the magnetic ion and (ii) the anisotropic exchange interaction between the magnetic ions in the 2D layer. The SIA of the Cr-based vdW ferromagnets is considered to be small because of the t_{2g}^3 configuration of the Cr^{3+} ion, which has no orbital degree of freedom, as discussed, e.g., by Lado and Fernández-Rossi [20]. On the contrary, first-principles estimates of exchange coupling by Xu *et al.* [21] have shown that the SIA and Kitaev-type anisotropic magnetic coupling in the Cr-based vdW ferromagnets are of comparable magnitudes and compete with each other. Furthermore, Kim *et al.* [22] have performed multisite cluster-model multiplet calculations and attributed the strong PMA of CrI_3 to an anisotropic exchange coupling between Cr atoms through the iodine $5p$ ligand orbitals, which

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has strong spin-orbit coupling (SOC). In fact, x-ray magnetic circular dichroism (XMCD) measurements at the iodine L_1 edge of CrI_3 have revealed a finite orbital magnetic moment of the I $5p$ electrons, implying the importance of the ligand p orbitals in the PMA of the vdW ferromagnets [23]. As for CGT, which shows a weaker PMA than CrI_3 , the situation is complicated and it is far from clear which of the SIA or the anisotropic exchange is responsible for the PMA [22,24].

In order to evaluate the contribution of the SIA of Cr to the magnetic anisotropy, XMCD studies at the Cr $L_{2,3}$ edge are expected to give essential information. So far Cr $L_{2,3}$ -edge XMCD has been reported for CGT [22,25] and CrI_3 [26] with a line-shape analysis using atomic-model and cluster-model calculations, and the contribution of the Cr $3d$ electrons to the PMA has been estimated [22] using the simple model proposed by Bruno [27]. In the present work, we have carried out Cr $L_{2,3}$ -edge XMCD measurements of a CGT single crystal under magnetic fields applied to different crystallographic directions and subsequent cluster-model multiplet calculations to directly estimate the SIA energy of the Cr atom centered in the CrTe_6 octahedron.

II. METHODS

Single crystals of CGT were synthesized using a flux method. High-purity Cr, Ge, and Te powders were mixed in a molar ratio of 2:6:36; the extra Ge and Te were used as a flux. The mixture was loaded in an alumina crucible and sealed in an evacuated quartz tube. A ball of alumina fiber was placed on top of the crucible. The quartz tube was placed in a furnace, heated to 700 °C, held for 5 h, and then slowly cooled down to 480 °C over a period of 3 days. This was followed by centrifugation to remove the flux.

X-ray absorption spectroscopy (XAS) and XMCD measurements at the Cr $L_{2,3}$ edge were performed at beamline BL23SU of SPring-8 and beamline BL-16A of Photon Factory at High Energy Accelerator Research Organization (KEK-PF). The measurement at SPring-8 was performed under a magnetic field of $\mu_0 H = 3$ T parallel to the c axis of the sample. The XAS and XMCD spectra were recorded in the total electron yield mode. Right (σ^+) and left (σ^-) circularly polarized x rays were switched at a frequency of 1 Hz in order to eliminate the time-dependent background from the obtained XMCD spectra. The sample temperature (T) during the measurement was set to 20 K, well below the Curie temperature. The sample was cleaved in the vacuum chamber prior to the measurements to obtain fresh surfaces. The magnetic field direction dependence of XMCD spectra was measured at the BL-16A of KEK-PF. Polarization switching was made at a frequency of 10 Hz. A magnetic field of $\mu_0 H = 1$ T was applied parallel and perpendicular to the c axis. Signals were recorded in the total electron-yield mode.

To investigate the electronic structure which contributes to the ferromagnetism, configuration-interaction cluster-model multiplet calculations have been conducted using the XTLS 8.5 package [28]. Figure 1(a) shows the crystal structure of CGT. Each Cr atom is surrounded by six Te atoms, forming a CrTe_6 cluster. It constitutes the CrGeTe_3 layer, which is stacked through vdW force. The CrTe_6 cluster is slightly elongated along the c axis [7], as shown in Fig. 1(b), which means

FIG. 1. Crystal structure of $\text{Cr}_2\text{Ge}_2\text{Te}_6$ (CGT). (a) Schematic drawing of the crystal structure. (b) CrTe_6 octahedron which is elongated along the c axis. (c) Crystal-field splitting of the Cr $3d$ orbital in the distorted octahedron to trigonal symmetry.

that the Cr electrons are under a nearly octahedral, trigonally distorted crystal field. The following parameters of the cluster model are used to reproduce the experimental XMCD spectra: the Cr $3d$ - $3d$ Coulomb energy U_{dd} , the Cr $2p$ - $3d$ Coulomb energy $U_{pd} \approx 1.2U_{dd}$, the charge-transfer energy Δ from the Te $5p$ to Cr $3d$ levels, the Slater-Koster parameter ($pd\sigma$) between the Cr $3d$ and Te $5p$ orbitals, the crystal-field splitting $10Dq$ (≈ 0.7 eV) between the Cr e_g and t_{2g} levels (in addition to the p - d covalency contribution), and the trigonal crystal-field splitting Dt between the a_{1g} and $e_{g\pi}$ orbitals. [For the definition of $10Dq$ and Dt , see Fig. 1(c).] As for the parameter values, we follow the empirical relationship [29] and employ $\Delta = 4.5$ eV, $U_{dd} = 6.0$ eV, and $(pd\sigma) = 2.6$ eV as being relevant to Cr^{3+} tellurides. The SOC parameter of the Cr $3d$ orbital is taken to be 35 meV.

III. RESULTS AND DISCUSSION

Figure 2 shows Cr $L_{2,3}$ -edge XAS and XMCD spectra of CGT under the out-of-plane magnetic field of $\mu_0 H = 3$ T at $T = 20$ K. The spectra are in good agreement with those reported in the Supplemental Material of Ref. [22] while there are some discrepancies of the XAS spectrum from those reported in Ref. [25], probably due to oxide contributions in the latter data [30,31]. The applied magnetic field was high enough to saturate the magnetization of CGT because the magnetization saturates below ~ 0.5 T [10]. The tail of the Te $M_{4,5}$ XAS peak overlapping the Cr $L_{2,3}$ XAS spectrum has been subtracted assuming a hyperbola. Arctangent steps at the L_2 and L_3 edges have also been subtracted from the

FIG. 2. Cr $L_{2,3}$ XAS and XMCD spectra of CGT at $\mu_0 H = 3$ T and $T = 20$ K. The red curve shows the average of XAS spectra obtained with left and right circularly polarized x rays. The green curve shows the XMCD spectrum, which is the intensity difference between the above two XAS spectra. The blue dotted curve shows the integral of the XMCD spectrum. Magnetic field is applied perpendicular to the sample surface ($H \parallel c$ axis), that is, along the easy magnetization axis.

Cr $L_{2,3}$ XAS as usual. On the other hand, the XMCD signals predominantly come from the magnetic Cr atoms, and there is no need to subtract signals from the Te atoms.

Figure 3 shows comparison of the measured Cr $L_{2,3}$ XMCD spectrum with those calculated using the cluster model assuming the Cr valences of 4+, 3+, 2+ high-spin states, and 2+ low-spin states. The experimental spectrum shows three negative peaks and one positive peak at the L_3 edge, and one negative peak and two positive peaks at the L_2 edge. The comparison shows that the calculation for the Cr^{3+} state reproduces the experimental spectrum better than those for the Cr^{2+} and Cr^{4+} states. Thus, one can conclude that the Cr atom in CGT is in the 3+ state (with the high-spin t_{2g}^3 configuration), and not in the 2+ nor 4+ state.

A. Spin and orbital magnetic moments

The orbital and effective spin magnetic moments are quantitatively estimated from the XAS and XMCD spectra using the XMCD sum rules [32,33]. For the $L_{2,3}$ edge ($2p \rightarrow 3d$ transition), the sum rules are given by

$$m_{\text{orb}} = -\frac{4n_h}{3} \frac{\int_{L_3+L_2} (\mu_+ - \mu_-) d\omega}{\int_{L_3+L_2} (\mu_+ + \mu_-) d\omega}, \quad (1)$$

$$\begin{aligned} m_{\text{spin}}^{\text{eff}} &= m_{\text{spin}} + \frac{7}{2} m_T \\ &= -2n_h \frac{\int_{L_3} (\mu_+ - \mu_-) d\omega - 2 \int_{L_2} (\mu_+ - \mu_-) d\omega}{\int_{L_3+L_2} (\mu_+ + \mu_-) d\omega}, \quad (2) \end{aligned}$$

where μ_+ (μ_-) is an XAS spectrum taken with σ^+ (σ^-), and m_{orb} , m_{spin} , and m_T are the orbital magnetic moment,

FIG. 3. Experimental and calculated Cr $L_{2,3}$ XMCD spectra of CGT. The experimental spectrum is the XMCD spectrum taken with magnetic field perpendicular to the ab plane. The orange, green, light-blue, and blue curves show XMCD spectra calculated using the cluster model with parameters which yield the Cr valences of 3+, 4+, 2+ high-spin (HS), and 2+ low-spin (LS) states, respectively. The used parameter values are $(\Delta, U, 10Dq) = (4.5, 6, 0.7)$, $(0, 5.2, 0.7)$, $(4.1, 4.2, 0.7)$, and $(4.1, 4.2, 2.1)$, respectively, in eV with $(pd\sigma) = 2.6$ eV fixed. An unusually large $10Dq$ or $(pd\sigma)$ was necessary to stabilize the LS state.

spin magnetic moment, and magnetic dipole moment, respectively, in units of Bohr magneton $\mu_B/\text{Cr atom}$. μ_+ (μ_-) stands for the absorption coefficient for photon helicity parallel (antiparallel) to the Cr majority spin direction. n_h is the number of holes in the valence shell. By applying the sum rules to the spectra in Fig. 2, the orbital magnetic moment of $m_{\text{orb}} = 0.00 \pm 0.05 \mu_B/\text{Cr atoms}$ has been obtained, consistent with the quenched orbital magnetic moment in the d^3 configuration of Cr^{3+} . The effective spin magnetic moment of $m_{\text{spin}}^{\text{eff}} \equiv m_{\text{spin}} + \frac{7}{2} m_T = 1.9 \pm 0.1 \mu_B/\text{Cr atom}$ has been obtained, where the m_{spin} and m_T are the spin magnetic moment and the magnetic dipole moment, respectively. Here, a correction factor of 1.7 has been applied to correct for the overlap of the L_2 - and L_3 -edge XMCD [34]. In a high-symmetry environment of the Cr atom as in CGT, m_T is negligibly small compared to m_{spin} [35,36]. Therefore, since m_{orb} is nearly zero, we regard $m_{\text{spin}}^{\text{eff}}$ as the total magnetic moment m_{spin} . The value $m_{\text{spin}} \sim m_{\text{spin}}^{\text{eff}} = 1.9 \pm 0.1 \mu_B/\text{Cr}$ is a little smaller than but consistent with the reported saturation magnetization of CGT, 2.2–2.9 $\mu_B/\text{Cr atom}$ [7,9,11].

B. Crystal-field splitting

In order to study the anisotropies of the electronic and magnetic properties of CGT, XMCD measurements under

FIG. 4. Experimental Cr $L_{2,3}$ XAS and XMCD spectra of CGT obtained with different magnetic field directions. (a) Red and black curves show XAS spectra taken with the out-of-plane and in-plane magnetic fields, respectively. (b) XMCD spectra under out-of-plane and in-plane magnetic fields. Red and black spectra show the out-of-plane and in-plane XMCD spectra, respectively. The strength of the magnetic field was 1 T and the measurement temperature was 50 K.

different magnetic field directions have been made. Figure 4 shows the Cr $L_{2,3}$ XAS and XMCD spectra taken with magnetic fields applied to the out-of-plane ($H \parallel c$ axis) and in-plane ($H \parallel ab$ plane) directions. The XMCD spectra show small but clear differences between the different magnetic field directions, while the spectral line shapes of the XAS spectra are relatively insensitive to the field direction, in agreement with the results reported by Kim *et al.* [22]. To identify the microscopic origin of the spectral differences between the different field directions, cluster-model multiplet calculations have been conducted assuming the Cr valence to be 3+. The effects of the elongation of the CrTe₆ octahedron along the c axis [7] are taken into account as a trigonal crystal-field splitting Dt of the t_{2g} level as shown in Fig. 1(c), where the triply degenerate t_{2g} level is split into the nondegenerate a_{1g} and doubly degenerate e_g^π levels. Here, for a positive (negative) trigonal crystal field Dt , the a_{1g} level is located above (below) the e_g^π level. Figures 5(b) and 5(c) show the calculated spectra without and with the trigonal crystal field, respectively, compared with experiment [Fig. 5(a)]. Without the trigonal crystal field, i.e., $Dt = 0$ eV [Fig. 5(b)], there is no difference in the XMCD spectra between the out-of-plane and in-plane magnetic fields. On the other hand, the calculated XMCD spectra under the trigonal crystal field Dt of 0.2 eV show finite differences between the out-of-plane and in-plane magnetic fields, as shown in Fig. 5(c), and well explain the experiment [Fig. 5(a)]. Thus, we conclude that the differences

FIG. 5. Experimental and calculated Cr $L_{2,3}$ XMCD spectra of CGT for different magnetic field directions. The red and black curves show XMCD spectra taken under magnetic fields perpendicular (out of plane) and parallel (in plane) to the surface, respectively. Blue curves show the difference between the XMCD spectra measured with different magnetic field directions. (a) Experimental XMCD spectra. (b), (c) XMCD spectra obtained by cluster-model calculations with and without the trigonal crystal field. Dt denotes the trigonal-field splitting. Clear differences in the line shapes between the different magnetic field directions are indicated by black arrows.

in the XMCD spectra taken with the different magnetic field directions are attributed to the elongation of the CrTe₆ octahedron along the c axis.

C. Magnetic anisotropy energies

SIA occurs if (i) the electronic structure is anisotropic (noncubic) and (ii) SOC is finite. If one of these two is missing, there will be no SIA. To evaluate the SIA of the Cr ion using the cluster model, the ground-state energy of the cluster is calculated for the different magnetic field directions. Thus, we find that the energy for the in-plane magnetic field is lower than the energy for the out-of-plane magnetic field by $\sim 5 \times 10^{-6}$ eV/Cr atom, that is, the SIA is opposite to the observed PMA. If we take parameter values used by Kim *et al.* [$U = 5.0$ eV, $\Delta = 1.0$ eV, $(pd\sigma) = 1.45$ eV, $10Dq = 0.8$ eV] [22], the in-plane magnetization has a higher energy

than the out-of-plane magnetization by $\sim 0.5 \times 10^{-6}$ eV/Cr, indicating a PMA much weaker than experiment. If ($p d \sigma$) is increased to our value (2.6 eV), the PMA becomes even weaker ($\sim 0.3 \times 10^{-6}$ eV/Cr). If $Dt = 0.2$ eV is introduced as in our calculation, in-plane magnetization is stabilized by $\sim 8.7 \times 10^{-6}$ eV/Cr. These calculated magnetic anisotropies using different parameters indicate that a large Dt value incorrectly predicts the sign of the SIA and does not lead to PMA. If Dt is reduced or neglected, PMA is correctly predicted but the anisotropy energy is one to two orders of magnitude smaller than the experimental value of $\sim 1\text{--}4 \times 10^{-5}$ eV/Cr atom [11,12], and the first-principles theoretical value of SIA, $\sim 3 \times 10^{-4}$ eV/Cr atom [17]. The application of the Bruno model [27] to the orbital-angular-momentum anisotropy has not been able to explain the PMA [22]. Those results agree with the first-principles calculation by Wang *et al.* [24] in that the SIA of Cr is weak and acts against PMA.

In spite of the large trigonal crystal field $Dt \sim 0.2$ eV and the resulting anisotropy in the XMCD spectra, the calculated magnetic anisotropy energy is small because of the high-spin t_{2g}^3 configuration, which has no orbital degree of freedom. Therefore, we consider that effects beyond the SIA evaluated using the cluster model, where only the spin-orbit coupling of the Co 3d electrons are taken into account, may play important roles in realizing the PMA of CGT. Such effects would include anisotropic exchange coupling between Cr ions through the ligand Te 5p electrons with strong SOC, in analogy to CrI₃. In the case of CrI₃, which has a stronger PMA than CGT, density functional theory (DFT) calculations [20,37] and multi-Cr site cluster-model multiplet calculations [22] have clearly shown that exchange coupling between Cr ions through I 5p orbitals explains the stronger PMA of CrI₃.

In addition to the SIA of Cr and anisotropic exchange between Cr discussed above, the magnetic anisotropy of the Te 5p electrons themselves may contribute to the magnetic anisotropy of CGT [24]. Such an anisotropy could arise because the Te 5p electrons are partially spin polarized due to hybridization with the Cr 3d electrons, in analogy to the magnetic anisotropy of the Pt 5d electrons in L1₀-type FePt [38,39]. In order to address this issue, further theoretical and experimental (XMCD at the Te absorption edges) studies would be necessary.

IV. CONCLUSION

We have performed XAS and XMCD measurements at the Cr $L_{2,3}$ edge and subsequent cluster-model calculations on CGT to investigate the electronic structure which contributes to the ferromagnetism and magnetic anisotropy. The effective spin magnetic moment obtained using the sum rules is $1.9 \mu_B/\text{Cr}$, consistent with previous reports, while the orbital magnetic moment is nearly zero. Subtle changes of the XMCD spectra are observed by changing the magnetic field direction, and are attributed to the distortion of the CrTe₆ octahedron from a comparison with the cluster-model calculation including the trigonal crystal field of the cluster elongated along the c axis. The magnetic anisotropy energy calculated using the cluster model is too small and has an opposite sign compared to experiment. This implies that the magnetic anisotropy of CGT cannot be explained by the SIA of Cr described by the cluster model, and that one has to take into account the interaction between Cr atoms through Te 5p ligands which have strong SOC.

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